

FR 1 283 831



PATENT SPECIFICATION

NO DRAWINGS

898.826

Date of Application and filing Complete Specification: May 11, 1959.

No. 16026/59.

Application made in Japan (No. 1140) on Jan. 16, 1959.

Complete Specification Published: June 14, 1962.

Index at acceptance:—Class 81(2), E1H.

International Classification:—A61L.

COMPLETE SPECIFICATION

Method for the preparation of Therapeutic Non-Adhesive, Ventilating Materials

I, NOBUHISA KAWAGUCHI, of Japanese nationality residing at 174, Sanya-cho Yoyogi, Shibuya-ku, Tokyo, Japan, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the preparation of therapeutic, non-adhesive ventilating materials.

The clinical treatment for wounded surfaces of skin inclusive of the application of medicaments requires three essential conditions, that is good ventilation, good absorption to body fluids, e.g. blood and pus, and the avoidance of physical damage. Unless these three conditions are fulfilled, it has been known that no favorable effect will result. For instance, tin foils, which have a good non-adhesive effect, are often used in grafting techniques though however having neither ventilating nor absorbing properties. Thus, tin foils have the disadvantage of retarding cure.

The petroleum jelly adopted by surgeons frequently, though it has a strong water-repelling property, will not disturb the ventilation, if used in a small quantity, notwithstanding that it is unsatisfactorily non-adhesive. If it is used in a large quantity, the non-adhesive property will become good, while the ventilating property will be lost. Sometimes, unfavorable secondary action will occur to a wounded part. Also its effect will be decreased due to the contamination with other medicines applied.

The present invention relates to a method for the manufacture of therapeutic, non-adhesive, ventilating materials, characterized in that polysiloxane coatings are formed and adhered on the surfaces of therapeutic and non-adhesive materials, in such a manner that their ventilating property is not disturbed; that is, according to the method of the present invention, all the foregoing disadvantages can be eliminated in the ventilating materials. In [Price 4s. 6d.].

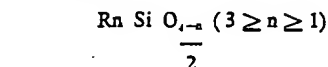
particular, an excellent therapeutic and good ventilating material can be provided, having an excellent absorptive property to a secretion, blood and pus and also being capable of being taken from the wounded portion without pain, by providing polysiloxane coatings on surfaces of porous gauzes for use on wounded surfaces of skin and inner organs, which are ulcerous.

Further more, the raw material gauze used in the method of the present invention can resist the chemical and physical process for forming polysiloxane coatings on the fibres forming said gauze. Any material can be used which is substantially unpoisonous, whatever kind it may be or in whatever colour it may be coloured or not coloured. However, staple fibres such as cotton or wool are inadequate, because fibres are liable to drop and remain in wounded surfaces. However, the gauze should be preferably synthetic resin, such as Nylon, polyethyleneterephthalate, polyacrylonitril rayon, cellulose acetate, and other cellulose esters, rayon fibres of the type of polyvinyl alcohol derivative, wherein the —OH radical in the molecule is partially substituted with —H, —CHO, —O.CO.CH, etc.; polyvinylformal type fibres (i.e. partially formalised polyvinyl alcohol) and viscose, or glass fabric. The porous gauzes also may be of woven or knitted fabric or hand-made Japanese paper, nylon paper, glass fibre and the like, and further porous and spongy materials.

The present invention may be applied to general surgical wound, hair-planting and grafting techniques, fire burns, etc. and an excellent non-adhesive property is found which diminishes the stimulus at the wounded portion to the minimum during the treatment and simultaneously decreases the destruction of granulation tissue during healing and decreases the bleeding also to a minimum, which advantageously shortens the period of cure.

Further, the polysiloxane used in the process of the present invention is a polymer

having a unit construction as represented by ing pores, by a known method. If necessary, it is applied uniformly onto fibers or porous sponges having numerous penetrating pores, alone either in the form of liquid or vapour or together with a non-poisonous catalyst or in a solvent solution or in an emulsion as dispersed in water or in the sprayed form, which is heated, if necessary, in order to accelerate the chemical reaction at a temperature, such that can be resisted by the fibers or sponges, but preferably at 90 to 200° C. However, according to the present invention, neither the catalyst nor the heating operation is essential and what is required is a chemical reaction (curing) of rendering the material infusible and insoluble. Such a chemical reaction can proceed even in the air, at ordinary temperatures. In such a treatment, other synthetic resin liquids, for instance, urea-formaldehyde resin for treating fibers, melanin resin, vinyl resin may also be used therewith. Likewise, surface-active substances can be used.



(wherein R represents a hydrogen atom or monovalent hydrocarbon radical, particularly alkyl or aryl radicals, such as methyl, ethyl, phenyl, cyclohexyl, or vinyl, or their combined and derived radicals.) When the polymer is heated alone on the fiber to be treated or together with a catalyst for making it infusible and insoluble, for instance, a heavy metal salt, such as an organic acid salt or halide (or oxyhalide) of zinc, tin, iron, cobalt, manganese, or zirconium, inorganic bases, and organic peroxides, ammonia, alkalies and organotinates, it becomes infusible and insoluble, particularly it becomes insoluble in water, ethyl alcohol, benzol, toluol, lower chlorinated hydrocarbons and dilute aqueous hydrogen peroxide solution, its contact angle to water being not less than 90°.

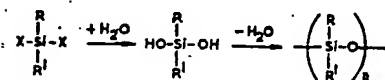
This material is mainly used for economic reason, in the form of an oily condensation product (or a polymer) as represented by a formula:



(wherein R represents CH_3 -, C_2H_5 - or C_6H_5 -, an oily condensation product (or a polymer) as represented by a formula:



or their mixtures or copolymers. However, a combination of such substances as subsequently produces the above kinds of materials resulting from hydrolysis and condensation reactions can of course be used with similar effects, provided that coatings of above-mentioned chemicals can be obtained thereby, said reaction being as in the following:



(wherein X represents a hydrolysable radical; such as halogen, alkoxy, etc. R, R¹ represents CH_3 , H, C_2H_5 , C_6H_5 , etc.)

The foregoing material is applied to fibers or porous sponges having numerous penetrat-

ing pores, by a known method. If necessary, it is applied uniformly onto fibers or porous sponges having numerous penetrating pores, alone either in the form of liquid or vapour or together with a non-poisonous catalyst or in a solvent solution or in an emulsion as dispersed in water or in the sprayed form, which is heated, if necessary, in order to accelerate the chemical reaction at a temperature, such that can be resisted by the fibers or sponges, but preferably at 90 to 200° C. However, according to the present invention, neither the catalyst nor the heating operation is essential and what is required is a chemical reaction (curing) of rendering the material infusible and insoluble. Such a chemical reaction can proceed even in the air, at ordinary temperatures. In such a treatment, other synthetic resin liquids, for instance, urea-formaldehyde resin for treating fibers, melanin resin, vinyl resin may also be used therewith. Likewise, surface-active substances can be used.

Further, according to the process of the present invention, the reason for the non-sticking property has not been established at present, because the cure mechanism of a cut or wound has not sufficiently been clarified. Materials of high water repellent property, such as paraffin, fat and oil do not show a good result, when used for the present purpose. This does not seem to arise merely from the water repellent and non-adhesive properties thereof. The main cause seems rather to be due to an inactiveness, in a broad sense of polysiloxane in contact with a living body, to materials like enzymes, steroids or lipoids contained in a body. This inactiveness is considered to be doubled by the water repellent property arising from the arrangement of hydrogen atoms on the surface of siloxane coatings.

Examples of embodiment of the present invention will be described in the following. However, this invention is not restricted by these examples.

EXAMPLE 1.

An oily substance of methylhydrogenpolysiloxane having trimethylsilane as an end radical was admixed with dimethylpolysiloxane having also an end radical of trimethylsilane and a viscosity at ordinary temperature of 100 poises, so that the molecular ratio Si H/Si (CH_3)₃ of said mixture was equal to 3.5/1; 10 parts of said mixed solution was dispersed in 90 parts of chloroform and then 0.2 parts of tin octoate were added thereto. A hand-woven fabric of glass fiber of approx. 7 mil thickness was dipped in said dispersed solution and then squeezed to approx. 1% of non-volatile matter (on dry basis) remaining as absorbed. A specimen having been obtained by heating same for about 10 minutes at 145° C. after the solvent was evaporated was applied to a wounded skin surface after grafting. The non-sticking property thereof was

then tested after a week. The specimen could be peeled off without pain and a considerable quantity of liquid containing blood secreted had been absorbed by the absorbing gauze (made of cotton) placed on the reverse side of the specimen. The healing effect was extremely good.

Further a coating has been formed on the glass fiber itself according to the above-mentioned method, which fibers are then woven into a porous substance which can be used with a similar effect.

EXAMPLE 2.

A piece of polyurethane sponge of approx. 10 mm thickness having an apparent specific gravity of 0.04 as well as perforations was sprayed with a 10% benzol solution of methyl hydrogen siloxane oil having a viscosity of about 0.5 poises at ordinary temperature, on both sides thereof to such an extent that said solution would not penetrate into the inner layer portion of the sponge. After being dried by air for about two hours, it was stood for 10 minutes in a thermostatic furnace kept at 150° C. to cause the siloxane to co-polymerize. Such a sponge was pressed on a wounded portion after hair-planting and was peeled off after one week. No adhesion was found at the wounded portion, peeling could be effected without pain, and the secreted liquid was well absorbed in the interior of the sponge.

EXAMPLE 3.

40 parts of oily methyl hydrogen polysiloxane having a viscosity of approximately 0.5 poises at ordinary temperatures were added to 60 parts of toluol-soluble, semi-fluid and viscous dimethyl polysiloxane having a Williams plasticity at 25° C. of approximately 50 mil. The Williams plasticity (ref. A.S.T.M. 1955, Part 6, page 950) was obtained by placing a fixed volume of sample between two discs, the lower one being fixed and the upper being movable vertically.

The upper disc is loaded for a given time, and the clearance between the discs measured with a dial gauge.

The material was dispersed in 400 parts of solvent naptha by means of a kneading machine. The mixture is designated as liquid specimen A. 0.5 parts of benzoyl peroxide were added to 100 parts of A and the whole dissolved in 5 times its volume of perchlorethylene. This was applied to a Japanese paper and heated at 120° C. for 4 minutes after drying in air for 30 minutes. The resulting specimen was found to peel off extremely satisfactorily when used in skin surgery.

EXAMPLE 4.

An emulsion comprising 100 parts of A, as described in Example 3, 10 parts of zinc octoate, 100 parts of trichlorethylene, 5 parts emulsifier and 210 parts water was made and a nylon taffeta was treated with the thus emulsified liquid, and thereafter the specimen was heated at 140° C. for 15 minutes. Such a

specimen proved to have an excellent non-sticking property as well as an extraordinarily good penetrability to secreting liquid, when the resulting specimen was used for a wounded surface of burnt skin.

EXAMPLE 5.

70 parts oily substance which was obtained by cohydrolysing and condensing the substance comprising 7 mol % of trimethyl chlorosilane and 93 mol % of methylhydrogendichlorosilane were emulsified together with 10 parts of such a methylphenyl polysiloxane as had a viscosity at ordinary temperatures of 150 poises, 10 parts benzol and 10 parts of ethylene tetrachloride by virtue of 8 parts of lauryl alcohol sulfonate and 192 parts of water as emulsifying agent. 30 parts of the thus obtained emulsion was admixed with 100 parts methylolmelamine resin for processing fibers and 300 parts water, in order to obtain a liquid. Zinc octoate emulsion containing approx. 4% zinc was added to the thus obtained liquid and a cloth of 3 mil thickness made of polyester fibre was dipped in said liquid, and then dried and thereafter heated at 160° C. for 3 minutes to obtain a specimen. When such a specimen was applied to a burnt surface, it showed an excellent non-sticking property. Further, the present specimen showed no decrease of its non-sticking property after being used once, if it were washed with warm water and soap and then dried and reused after being sterilized at 120° C. with pressure steam.

EXAMPLE 6.

Acetate tricot knitted fabric was so treated with a liquid comprising about 7 parts oily diethyl polysiloxane of about 5 poises viscosity at room temperature, 0.3 parts methyl vinyl polysiloxane, 0.1 part tetrabutyl titanate and 150 parts methylene chloride, that non-volatile matter attached to said cloth was about 3.75 % based on the dried weight of the cloth. Thus treated wet cloth was dried at an ordinary temperature in air for 72 hours. When the resulting cloth was used on an operation wound, an excellent non-sticking property was obtained.

EXAMPLE 7.

A polyurethane sponge 3 mm thickness having an apparent specific gravity of 0.04, which absorbed moisture sufficiently in a chamber of 100 % Relative Humidity, was allowed to stand in the vapour of methylhydrogendiothoxysilane, then said polyurethane sponge was withdrawn after 25 hours elapsed, and was heated at 120° C. for 20 minutes to obtain a porous sponge. When such a sponge was used for applying pressure in dermatological surgery, it showed an excellent non-sticking property.

EXAMPLE 8.

A glass fiber hand-woven fabric having a thickness of approximately 7 mil, which was sterilized at first and then moistened, was

kept for one hour in the vapor of a mixture of dimethyl dichlorosilane and methyl trichlorosilane in a molecular ratio of 2:3, and was removed approximately 1 hour later and heated at 220° C. for 4 hours. An excellent non-sticking property was shown by the thus obtained specimen, when used for a surgical skin wound.

WHAT I CLAIM IS:—

1. A method for the preparation of therapeutic, non-adhesive ventilating materials, characterised in that an organo-polysiloxane film is caused to be secured on the surfaces of the ventilating material in such a manner that the ventilating property thereof is not disturbed.

2. A method as claimed in claim 1 wherein the organosiloxane is a polymer or condensation product having a unit construction represented by $R_n Si O_{\frac{n}{2}}$ wherein R represents a

hydrogen atom or a monovalent hydrocarbon radical, such as methyl, ethyl, phenyl, cyclohexyl, vinyl, or their combined and derived radicals, and wherein $3 \geq n \geq 1$.

3. A method as claimed in claims 1 and 2 wherein said ventilating materials are treated with a combination of organosiloxane and

amide-type condensed resin or vinyl-type polymerised resin.

4. A method as claimed in claims 1, 2 and 3 wherein said organosiloxane coating is formed on the fibre before weaving, knitting, or other method of manufacture, such that a ventilating material may be obtained.

5. A method as claimed in claims 1, 2, and 4 wherein the ventilating material is nylon, polyethylene-terephthalate, polyacrylonitril rayon, viscose, material made from polyvinyl alcohol derivative fibres as hereinbefore described, cellulose acetate, polyurethane sponge, glass fabric, or Japanese hand-made paper.

6. A method for the preparation of therapeutic, non-adhesive ventilating materials as claimed in claims 1, 4 and 5, wherein the ventilating material is coloured.

7. Therapeutic, non-adhesive, ventilating materials prepared in accordance with any of the methods claimed hereinbefore.

8. Therapeutic, non-adhesive, ventilating materials substantially as hereinbefore described.

MARKS & CLERK,
Chartered Patent Agents,
Agents for the Applicant(s).

Leamington Spa: Printed for Her Majesty's Stationary Office, by the Courier Press.—1962.
Published by The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

BEST AVAILABLE COPY